Million-fold acceleration of a Diels-Alder reaction due to combined Lewis acid and micellar catalysis in water

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Supporting Information

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Derivation of equation (1)

Assuming complete binding of the dienophile to the micelle and making use of the pseudophase model, one can derive an expression relating the observed pseudo-first-order rate constant k_{obs} to the concentration of surfactant, [S]. Assuming a negligible contribution of the reaction in the aqueous phase to the overall rate, the second-order rate constant in the micellar pseudophase k_m is now given by the following equation:

$$k_m = \frac{k_{obs}}{[\mathbf{2}]_m} \qquad A1$$

Next we express $[\mathbf{2}]_m$ as a function of the partition coefficient P_2 and the concentration of surfactant in the equation:

$$P_2 = \frac{[\mathbf{2}]_m}{[\mathbf{2}]_w} \qquad A2$$

$$[\mathbf{2}]_w = \frac{n_{2,w}}{V_w} = \frac{n_{2,t} - n_{2,m}}{V_w} = \frac{n_{2,t} - [\mathbf{2}]_m \cdot V_m}{V_w} \qquad A3$$

Where $n_{2,w}$, $n_{2,m}$ and $n_{2,t}$ are, respectively, the number of moles of **2** in the aqueous phase, the micellar phase and the total of the two. V_w and V_m are the volumes of the aqueous phase and the micellar pseudophase[1].

Substitution of *A2* in *A3* and solving for $[\mathbf{2}]_m$ gives:

$$\frac{1}{[\mathbf{2}]_m} = \frac{V_w}{P_2 \cdot n_{2,t}} + \frac{V_m}{n_{2,t}} \qquad A4$$

The volume of the micellar pseudophase can be estimated from the molar volume of the micellized surfactant $V_{mol,S}$:

$$V_m = ([S] - cmc) \cdot V_t \cdot V_{mol,S} \qquad A5$$

Substituting *A5* in *A4* and substituting $n_{2,t}$ with $[\mathbf{2}]_t \cdot V_t$ yields:

$$\frac{1}{[\mathbf{2}]_m} = \frac{V_w}{P_2 \cdot [\mathbf{2}]_t \cdot V_t} + \frac{([S] - cmc) \cdot V_{mol,S}}{[\mathbf{2}]_t} \qquad A6$$

Combining *A6* and *A1* gives the final equation with which k_m and P_2 can be obtained by plotting $[\mathbf{2}]_t/k_{obs}$ versus [S].

$$\frac{[\mathbf{2}]_t}{k_{obs}} = \frac{V_{mol,S}}{k_m} \cdot [S] + \frac{V_w}{P_2 \cdot V_t \cdot k_m} + \frac{cmc \cdot V_{mol,S}}{k_m} \qquad A7$$

Note

1) Inevitably, the estimate of a molar volume of the micellized surfactant that is available for solubilization is somewhat arbitrary.